Electronic Supplementary Information (ESI) for

Colloidal stability dictates drop breakup under electric fields

Javier A. Lanauze,[a‡] Rajarshi Sengupta,[a‡] Blake J. Bleier,[a] Benjamin A. Yezer,[a] Aditya S. Khair[a] and Lynn M. Walker*[a]

[a] *Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA. E-mail: lwalker@andrew.cmu.edu*

Boundary integral computations with insoluble surfactant

The procedure to evaluate the transient drop shapes is to sequentially solve for the electric field inside and outside the drop, and fluid flow inside and outside the drop, with interface conditions accounting for stress balance, charge conservation and surfactant transport.

Electric field

The drop and medium phases are weakly conducting and electrically neutral. Hence, Gauss's law for electrostatics reduces to the Laplace equation in the electrostatic potential, giving in dimensionless form $\nabla^2\phi_{i,o} = 0$, and the electric field is given by $\boldsymbol{E_{i,o}}=-\boldsymbol{\nabla}\phi_{i,o}$.[1–3] The subscripts denote the drop (i) and medium (o) phases, respectively. The electric field in the medium approaches the external applied electric field at large distances from the drop, along with the interface conditions,[2–4]

$$E_{t,o} = E_{t,i}, \tag{1}$$

and

$$E_{n,o} - SE_{n,i} = q, \tag{2}$$

where the subscripts t and n denote the tangential and normal components of the electric field respectively, q is the surface charge density, and $S = \varepsilon_i/\varepsilon_o$ is the permittivity ratio between the drop and medium phases. The Laplace equation can be recast into a non-dimensional integral equation, which can be simplified using interface condition (2) to[3, 4]

$$\frac{S-1}{4\pi S}\oint_A \frac{\boldsymbol{r}\cdot\boldsymbol{n}(\boldsymbol{x})}{r^3}E_{n,o}(\boldsymbol{y})dA(\boldsymbol{y})+\frac{S+1}{2S}E_{n,o}(\boldsymbol{x}) = \boldsymbol{E_\infty}\cdot\boldsymbol{n}(\boldsymbol{x})-\frac{1}{4\pi S}\oint_A q(\boldsymbol{y})dA(\boldsymbol{y})+\frac{1}{2S}q(\boldsymbol{x}). \quad (3)$$

Here, $\boldsymbol{r}=\boldsymbol{y}-\boldsymbol{x}$ is the distance between an observer point $\boldsymbol{y}$ that can move along the interface, and a source point $\boldsymbol{x}$ on the interface (figure 1).

The tangential component of the electric field is solved by an integral transformation of the Laplace equation in terms of the electrostatic potential and using $\boldsymbol{E_{i,o}}=-\boldsymbol{\nabla}\phi_{i,o}$. The integral equation to be solved is[3, 4]

$$\phi_o(\boldsymbol{x}) = \phi_\infty(\boldsymbol{x}) + \oint_A \frac{1}{4\pi r}(E_{n,o}(\boldsymbol{y}) - E_{n,i}(\boldsymbol{y}))dA(\boldsymbol{y}). \quad (4)$$

The interface is initially uncharged, hence the electric field can be calculated at $t = 0$. After evaluating the electric field, the jump in electric traction at the interface is computed using

$$[\boldsymbol{\tau_e}\cdot\boldsymbol{n}] = \frac{1}{2}[(E_{n,o}^2 - SE_{n,i}^2) + (S-1)E_{t,o}^2]\boldsymbol{n} + E_{t,o}(E_{n,o} - SE_{n,i})\boldsymbol{t}, \quad (5)$$

where $\boldsymbol{\tau}_{e(i,o)} = \boldsymbol{E}_{i,o}\boldsymbol{E}_{i,o} - E_{i,o}^2\boldsymbol{I}/2$ is the dimensionless form of the Maxwell stress tensor, and $\boldsymbol{t}$ is the unit vector along the tangential direction.

Fluid flow

The tangential component of the electric traction drives a fluid flow. We assume creeping flow in this study, and use the Stokes equations to compute the flow field. The integral representation of the Stokes equations in dimensionless form is given by[3]

$$\boldsymbol{u_o}(\boldsymbol{x}) = -\frac{1}{4\pi(M+1)}\oint_A \Delta\boldsymbol{f}(\boldsymbol{y})\cdot\boldsymbol{J}(\boldsymbol{y},\boldsymbol{x})dA(\boldsymbol{y}) - \frac{1}{4\pi}\frac{M-1}{M+1}\oint_A \boldsymbol{u_o}(\boldsymbol{y})\cdot\boldsymbol{K}(\boldsymbol{y},\boldsymbol{x})\cdot\boldsymbol{n}(\boldsymbol{y})dA(\boldsymbol{y}), \quad (6)$$

where $\boldsymbol{J}$ and $\boldsymbol{K}$ denote the free-space Green's functions for velocity and stress,[3] respectively, $M = \mu_i/\mu_o$ is the viscosity ratio between the drop and medium phases, and

$$\Delta \boldsymbol{f} = \frac{2\kappa}{Ca_o}\boldsymbol{n} - \frac{1}{Ca_o}\boldsymbol{\nabla_s}\gamma - [\boldsymbol{\tau_e}\boldsymbol{\cdot}\boldsymbol{n}] \tag{7}$$

is the jump in hydrodynamic traction at the interface, where κ is the mean curvature,[4] and γ denotes the interfacial tension.

Interfacial charge conservation

The surface charge density is updated after obtaining the interfacial velocity using[5,6]

$$\frac{1}{R}E_{n,i} - E_{n,o} = Sa_o\frac{\partial q}{\partial t} + Re_o\,\boldsymbol{\nabla_s}\boldsymbol{\cdot}\,(\boldsymbol{u}_s q), \tag{8}$$

where, $R = \chi_i/\chi_o$ is the ratio of resistivity between the drop and medium phase, the Saville number[5] $Sa_o = \tau_{e,o}/\tau_{c,o}$, represents a ratio of the charging timescale $\tau_{e,o} = \varepsilon_o\chi_o$ to the capillary timescale $\tau_{c,o} = \mu_o a/\gamma$, and the electric Reynolds number[7] $Re_o = \tau_{e,o}/\tau_f$, which represents a ratio of the charging timescale to the flow timescale $\tau_f = a/U$. The first term in the right hand side represents transient charging of the interface, and the second term denotes the convection of surface charge by the induced flow.

Interfacial surfactant transport

Next, the surfactant distribution at the interface is updated using a convection-diffusion equation,[8]

$$\frac{1}{Ca_o}\frac{\partial \Gamma}{\partial t} + \boldsymbol{\nabla_s}\boldsymbol{\cdot}(\boldsymbol{u_s}\Gamma) + (\boldsymbol{u_s}\boldsymbol{\cdot}\hat{\boldsymbol{n}})\kappa\Gamma - \frac{1}{Pe_s}\nabla_s^2\Gamma = 0. \tag{9}$$

Here, Γ is the surfactant concentration at the interface made dimensionless by the maximum surfactant coverage at the interface (Γ_∞), κ is the curvature, and $Pe_s = \dfrac{a^2\varepsilon_o E_\infty^2}{D_s\mu_o}$ is the surface Peclet number, which denotes the rate of surfactant transport by convection to diffusion along the interface, D_s being the surface diffusion coefficient. In (9), the second term represents the convection of surfactant by the flow, the third term denotes changes in surfactant concentration due to dilation of the interface, and the last term represents the lateral diffusion of surfactant along the interface. The surfactant is initially distributed uniformly at the interface. The interfacial tension, γ, is related to Γ through an equation of state. We use the von Szyskowski equation of state,

$$\gamma = \gamma_0 + E \ln(1 - \Gamma), \tag{10}$$

where γ_0 is the interfacial tension in the absence of surfactant, and the elasticity number, $E = \dfrac{RT\Gamma_\infty}{\gamma_{eq}}$ is a measure of the sensitivity of the interfacial tension to Γ, R is the universal gas constant, and T is the temperature. The interfacial tension has been non dimensionalised by the equilibrium interfacial tension value in the presence of surfactant, γ_{eq}. The equation of state permits the rewriting of the stress balance condition (7) in terms of the surfactant concentration as

$$\Delta \boldsymbol{f} = \frac{2\kappa}{Ca_o}\boldsymbol{n} - \frac{Ma}{1-\Gamma}\boldsymbol{\nabla_s}\Gamma - [\boldsymbol{\tau_e}\cdot\boldsymbol{n}], \tag{11}$$

where, $Ma = E/Ca_o$ is the Marangoni number which represents the ratio of Marangoni stresses to viscous stresses.

Finally, the interface is updated using the kinematic condition

$$\frac{d\boldsymbol{x}}{dt} = Ca_o(\boldsymbol{u_s}\cdot\boldsymbol{n})\boldsymbol{n}. \tag{12}$$

Numerical scheme

Equations (3), (4) and (6) are sequentially solved using the boundary integral method. The details of the numerical method have been discussed in detail by previous publications from our group,[3,4] and only reviewed here. The field and flow are assumed to be axisymmetric, which allows an analytical integration over the azimuthal direction, reducing surface integrals to line integrals over the contour of the drop. The top half of the drop is divided into N elements, creating $N + 1$ nodes. The nodes are called source points, and their coordinates are denoted by $\boldsymbol{x}$ (figure 1). All variables of interest are interpolated as cubic splines with respect to the arc length, s. The integral over the contour of the drop is expressed as a sum of integrals over each element. Singular terms in the integrand are subtracted out, and then added back, following standard regularization techniques.[9] The integrals are evaluated using Gauss-Legendre quadrature. The points at which the integral are evaluated are referred to as observer points, and their coordinates are denoted by $\boldsymbol{y}$. After the electric field and fluid flow is calculated, the surface charge density (8), surfactant concentration (9), interfacial tension (10) and shape of the interface (12) are updated using the second-order Runge-Kutta method. Then, the deformation of the drop is calculated at every time instant. The time step and N is chosen to ensure that the volumetric flow rate across the interface, which should identically be zero to conserve mass, is at most $\mathcal{O}(10^{-6})$ for the initial 20 iterations. This ensures numerical stability of the computations. If the volumetric flow rate across the interface remains $\mathcal{O}(10^{-6})$ or less, while the maximum value of the radial velocity keeps on decreasing, and reaches $\mathcal{O}(10^{-4})$ or less, we conclude that the drop has attained a steady shape. If the volumetric flow rate slowly starts to increase, along with an increase in the maximum value of the radial velocity, we conclude that the drop shape will be unsteady, and it will break up. The boundary integral method cannot track the interface after the drop breaks, and in this case, the results are reported at a time instant very close to breakup, where the ratio of volumetric flow rate across the interface to the initial volumetric flow rate is around $\mathcal{O}(10^2)$.

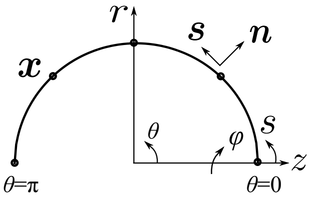

Figure 1: Schematic of discretization of the undeformed drop.

References

[1] H. A. Stone, J. R. Lister, and M. P. Brenner. Drops with conical ends in electric and magnetic fields. *Proc. R. Soc. London, Ser. A*, 455:329–347, 1999.

[2] E. Lac and G. M. Homsy. Axisymmetric deformation and stability of a viscous drop in a steady electric field. *J. Fluid Mech.*, 590:239–264, 2007.

[3] J. A. Lanauze, L. M. Walker, and A. S. Khair. Nonlinear electrohydrodynamics of slightly deformed oblate drops. *J. Fluid Mech.*, 774:245–266, 2015.

[4] Rajarshi Sengupta, Lynn M Walker, and Aditya S Khair. The role of surface charge convection in the electrohydrodynamics and breakup of prolate drops. *Journal of Fluid Mechanics*, 833:29–53, 2017.

[5] D. A. Saville. Electrohydrodynamics: the Taylor-Melcher leaky dielectric model. *Annu. Rev. Fluid Mech.*, 29:27–64, 1997.

[6] Charles D Eggleton, Yashodhara P Pawar, and Kathleen J Stebe. Insoluble surfactants on a drop in an extensional flow: a generalization of the stagnated surface limit to deforming interfaces. *Journal of Fluid Mechanics*, 385:79–99, 1999.

[7] J. R. Melcher and G. I. Taylor. Electrohydrodynamics: a review of the role of interfacial shear stresses. *Annu. Rev. Fluid Mech.*, 1:111–146, 1969.

[8] HA Stone. A simple derivation of the time-dependent convective-diffusion equation for surfactant transport along a deforming interface. *Physics of Fluids A: Fluid Dynamics*, 2(1):111–112, 1990.

[9] C. Pozrikidis. *A practical guide to boundary element methods with the software library BEMLIB.* CRC Press, 2010.